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L-Malic Acid as By-product in Apple Sirup Manufactured by Ion Exchange

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The *L*-malic acid which is adsorbed on an anion exchanger in the preparation of a bland apple sirup can be recovered from the effluent from the sodium carbonate regeneration of the exchanger. Only a slight modification is necessary in the regular regenerative procedure to re-

cover what would otherwise be waste material. The acid is obtained in the regenerant effluent as the soluble sodium salt, precipitated as the normal calcium salt, and converted to the free acid by double decomposition with sulfuric acid.

A PREVIOUS paper (4) described a procedure for the removal of malic acid from apple juice by adsorption on an anion exchanger used in the manufacture of apple sirup. Deacidification results in a lower requirement of lime for the precipitation of pectin than in the original sirup process (12), leaves less calcium malate in the juice, and produces a blander sirup. The present paper describes a procedure whereby the malic acid can be obtained as a by-product from the deacidification step in the manufacture of this type of apple sirup. Malic acid can be used as a food acidulant, and the active acid might also have special application in chemistry, where an optically active compound is desired.

It is generally recognized that *L*-malic acid (levorotatory) is the principal organic acid in apples, although the presence of citric acid has been reported (2, 7, 14). The absence of other acid simplifies the procedure, since it is not necessary to separate acids. No evidence of an acid other than *L*-malic was found in the apple juice used in the experiments reported herein. Charley *et al.* (5) prepared malic acid as a by-product in the manufacture of apple treacle. They neutralized the excess acidity of the juice with calcium carbonate and, on concentrating, obtained a precipitate of neutral calcium malate. Juice of high acidity (0.7%) was used in their work. The present authors were unable to duplicate their results with juices of a lower acidity (0.4%) commonly found in America. Active *L*-malic acid has also been prepared from maple sugar sand (18) and mountain ash berries (20).

Anion exchangers have been used in the recovery of tartaric acid from grape wastes (10). In the present work the anion exchanger is used as an acid adsorber, inasmuch as the main purpose is the reduction of the acidity of apple juice. Regen-

eration is accomplished with sodium carbonate solution, and the acid is recovered in the regenerant effluent as the soluble sodium salt and is precipitated from the effluent as the insoluble calcium salt.

Free malic acid is very difficult to crystallize. The apple sirup manufacturer would probably prefer to sell the calcium malate to chemical manufacturers, who in turn would prepare the free acid, either in crystalline form or as a concentrated solution.

It was also thought that the distillery waste from apple brandy manufacture might be utilized as another source of malic acid. However, analysis has shown that such wastes contain little, if any, malic acid. Malic acid is partially or completely destroyed during the fermentation process, probably being converted to lactic acid (8).

DETERMINATION OF MALIC ACID

Since malic was the only acid in the apple juice used in these studies and since it existed almost entirely in the uncombined condition (2), determination of the titratable acidity of apple juice gave its malic acid content. The juice was titrated with standard alkali to a pH value of 8.1 (3) rather than to a phenolphthalein end point. The latter is difficult to read because of the color of the juice and because of the appreciable darkening which occurs as the acid is neutralized.

The method generally employed for determination of sodium malate in the regenerant effluent is based on the fact that malic acid with a uranyl salt forms a complex with greatly increased rotatory power (6, 9, 21). Many modifications have been described in the literature. The one described here is a simplified A.O.A.C. procedure (1), since no other optically active substances are present in appreciable quantities. Analysis has shown that there is no sugar in the regenerant effluent.

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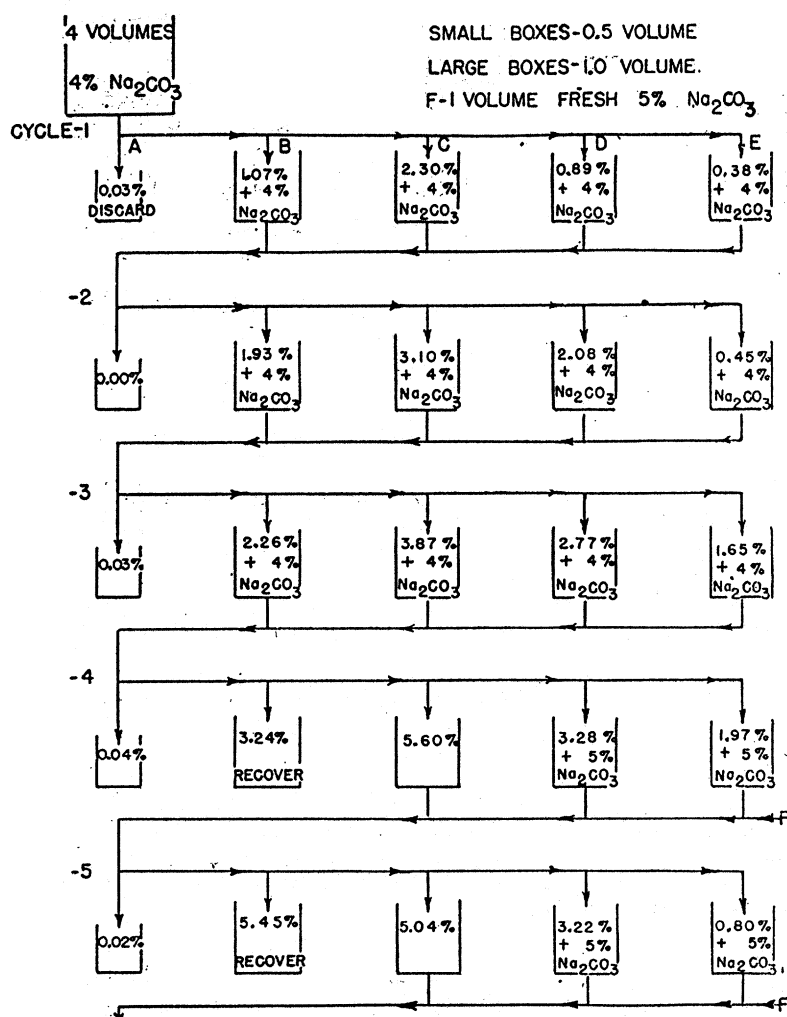


Figure 1. Method of Recycling Regenerant for Recovery of Malic Acid
Upper percentage indicates malate content

The procedure is briefly as follows: Pipet a 25-ml. sample into a 100-ml. volumetric flask; make it just alkaline to a phenolphthalein end point with 1 *N* sulfuric acid or 1 *N* sodium hydroxide; add 2 ml. glacial acetic acid and make to volume; transfer a 20-ml. aliquot to a 25-ml. volumetric flask containing approximately 3.0 grams of uranyl acetate (finely ground); shake vigorously at intervals for 3 hours; make to volume with saturated uranyl acetate solution and filter; polarize in a 200-mm. tube with sodium light. Calculation: degrees angular rotation $\times 0.519$ = grams malic acid per 100 ml. of original solution.

The accuracy of the method varies, but the results are considered sufficiently reliable to estimate the malate content of the regenerant effluent. For determining the purity of the precipitated calcium malate, the authors have relied on calcium and ash determinations. Comparison of the two methods of analysis on samples of calcium malate shows that the polarimetric method gives results which may vary as much as $\pm 5\%$ of those obtained by calcium and ash determinations.

ADSORPTION ON ANION EXCHANGER

General methods for the use of ion exchangers (13, 15, 16, 19) and their particular application to the deacidification of apple juice have been described in detail elsewhere (4). The screened (200 mesh) juice is passed downflow through an anion exchanger bed until the pH value of the combined effluent juice reaches 5.0; at this point about 80-85% of the malic acid in the juice processed has been adsorbed, and the exchanger is considered

exhausted. Exchanger beds of 1- and 4-inch diameters were used.

The capacity of the anion exchanger used about 15 volumes of juice, of approximately 0.4 malic acid content, per volume of exchanger; this represents an adsorption of about 750 milliequivalents, or approximately 50 grams, of malic acid per liter of exchanger. Variations in capacity from 650 to 850 milliequivalents per liter have been noted for the same exchanger with different juices. The anion exchanger used was De-Acidite (The Permutit Company), although other exchangers will work equally well.

REMOVAL FROM ANION EXCHANGER

After the exhaustion of the exchanger, the bed is backwashed with water to remove residual juice and then regenerated with sodium carbonate solution in preparation for the next cycle. The acid is removed from the exchanger in the regenerant effluent as the soluble sodium salt.

The original regenerant consists of 4 volumes of 4% sodium carbonate solution and is passed downflow through the exchanger bed at a rate of 2 gallons per minute per square foot of cross sectional area of the bed. The volume of regenerant used is expressed in terms of the volume of the bed. As the regenerant passes through the bed, most of the malate is eluted in the first portion of the effluent as shown in Figure 1, in which the percentages indicate the malate concentration in the effluent fractions. The first 0.5 volume of effluent (fraction A) is discarded, since it is largely the water displaced from the bed and contains little, if any, malate.

The regenerant effluent is recycled in order to build up the malate concentration to about 5%, at which point satisfactory precipitation of calcium malate can be obtained. A flow diagram for recycling the regenerant is illustrated in Figure 1. After discarding fraction A, four 1-volume fractions of effluent are collected from each cycle. Water is then passed through the bed to rinse out the excess alkali, and the bed is then ready for the deacidification of apple juice in the next cycle. The regenerant effluent fractions from cycle 1, after fortification with more sodium carbonate, are then passed through the exchanger bed in order as the regenerant for cycle 2. This procedure is repeated until the malate concentration in fraction B has reached the desired value, and B is then removed for recovery. The remainder of the fractions are used as the regenerant for the next cycle with the addition of one volume of fresh 5% sodium carbonate solution as shown in the diagram for cycle 4. From this point on, fraction B, which was fraction C in the preceding cycle, is withdrawn for precipitation.

After cycle 4, fraction C is not fortified with more sodium carbonate, since it already contains an excess, and passage through the exchanger in the next cycle reduces this excess so that there is less carbonate to remove in the precipitation procedure. The slight reduction of malate content from fraction C, cycle 4, to fraction B, cycle 5, is probably due to dilution by water in the exchanger which more than offsets the gain derived from a succeeding elution. The rinse water used after fraction E has been collected may contain small amounts of malate, and the first portion of this rinse water may be used for preparing the fresh sodium carbonate solution.

An excess of sodium carbonate is used to ensure complete removal of the adsorbed acid and to take care of the previously noted variation in the capacity of the exchanger for different

Smaller amounts of sodium carbonate did not always give complete recovery. The presence of inorganic anions from apple juice will increase the requirement of regenerant over that necessary to remove the adsorbed acid. No attempt was made to use an alkali stronger than sodium carbonate as a regenerant.

PRECIPITATION OF CALCIUM MALATE

The portion of the regenerant effluent saved for recovery contains about 5.0% malic acid as the soluble sodium salt in a solution containing an excess of sodium carbonate. The excess carbonate is removed by acidifying with hydrochloric acid. The malate is precipitated from this solution as the relatively insoluble neutral calcium salt.

While neutral calcium malate has limited solubility (20°, 0.82; 57°, 0.57 gram per 100 grams water), it does not precipitate so readily as might be expected. It is not precipitated from alkaline solution, and at too high acidity the more soluble calcium acid malate (20°, 1.5; 57°, 32.2 grams per 100 grams water) is formed, and the yields are lowered appreciably.

The complete procedure for precipitation of the neutral salt is described in detail with a specific example, and the factors affecting the precipitation will be discussed separately: Four liters of regenerant effluent with a pH value of 8.5 and containing 188 grams of malic acid as sodium malate were acidified with hydrochloric acid to a pH of 5.5. This solution was concentrated under vacuum to one fourth the original volume, and the pH value was adjusted to 6.0 with sodium hydroxide. A 40% calcium chloride solution was added slowly with stirring; 10% excess of calcium over the theoretical amount required was used. Usually a grainy precipitate formed immediately. Occasionally it was necessary to seed the supersaturated solution. This was allowed to stand for 24 hours for complete precipitation, and then was filtered by suction and washed with a small amount of hot water. The calcium malate was dried to constant weight at room temperature. The yield was 284 grams of dry product. Calcium determination proved this product to be 97% calcium malate as the trihydrate, and ash determination indicated that it contained 2% ash other than calcium. The yield represented a 90% recovery of the malate from the original regenerant effluent. Drying at 70° C. in a vacuum oven gave a hydrated product containing 1.5 molecules of water.

Figure 2 shows the effect of the malate concentration in the effluent on the yields of calcium malate obtained when precipitated at a pH value of 6.0. The effluent should be concentrated to 15 to 20% malate in order to realize a 90% recovery.

Figure 2 also shows that maximum recovery was obtained when precipitation occurred at an initial pH value of 6.0. Below 5.5 there was an appreciable decrease in yield, probably because of the formation of the more soluble acid salt. The pH value of the mother liquor after the precipitation is decreased to about 4.0. Maintaining the pH value at 6.0 during the precipitation does not increase the yield.

The acid salt can readily be obtained in good yields and with high purity by dissolving the neutral salt in a 10% nitric acid solution until saturated at 57° C., the temperature of maximum solubility. The saturated solution is filtered hot, and, on cooling, a fine white crystalline material separates. The crystalline calcium acid malate is the hexahydrate, and equivalent weight determinations indicate that a product of nearly 100% purity is obtained on the first crystallization.

CONVERSION OF CALCIUM MALATE TO MALIC ACID

The acid or neutral calcium malate can readily be converted to the free acid by treating it with sulfuric acid. The calcium is removed as insoluble sulfate. As might be expected from such a reaction, nearly quantitative yields can be obtained. Crystallization of the free acid from its solution, however, is not so easy.

The finely ground calcium malate is dispersed in about twice its weight of water to form a thick slurry, and 50% sulfuric acid is slowly stirred in. Slightly less than the calculated amount of sulfuric acid required to remove the calcium is used. The mixture is stirred for several hours, allowed to stand overnight, and then filtered on a suction filter. The precipitated calcium sulfate is washed with water, and the filtrate and washings are combined. On concentrating this dilute solution under vacuum, a further slight precipitate of calcium sulfate is formed; this is filtered off, and the filtrate is further concentrated to a thick sirup. For example, 150 grams of calcium malate trihydrate containing 87 grams of malic acid by analysis yielded 84 grams of malic acid as a 67% solution. This represents a 96% recovery of the acid from the calcium salt.

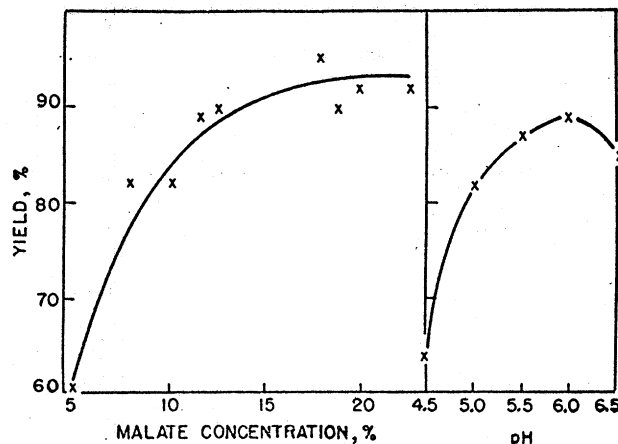


Figure 2. Effect of Malate Concentration and Initial pH of Precipitation on Yields of Calcium Malate

Because of its high solubility, malic acid is difficult to crystallize from its solution. Other workers have stated that crystallization will occur after the acid has been concentrated to a thick sirup and allowed to stand, but we have been unable to obtain a crystalline product. Drying at 70° C. in a vacuum oven does not cause crystallization, and no crystals have been obtained even on holding the thick sirup for long periods of time in a vacuum desiccator. The acid should not be dried at temperatures higher than 70° C. because of the possibility of anhydride formation (11).

For identification purposes, a small amount of crystalline *l*-malic acid was prepared by precipitation of the lead salt and subsequent decomposition with hydrogen sulfide to remove the lead. The resulting solution was concentrated in vacuo, and the residual water removed by distillation with absolute ethanol. A crystalline product was obtained, and this was recrystallized from an alcohol-benzene solution, which was evaporated until crystallization occurred. The material melted at 103° C. (corrected), which agrees with that reported by McCall and Guthrie (9). The mixed melting point with a known sample of *l*-malic acid was 103° C. The equivalent weight was 67.1 (calculated, 67.0). The melting point of the *p*-bromophenacyl ester was 179° C. (corrected), which agrees with that given by Shriner and Fuson (17).

DISCUSSION

l-Malic acid can be produced as a by-product in the manufacture of apple sirup by the ion exchange process. By a slight modification in the regular exchanger regenerative procedure with sodium carbonate, the acid is obtained as the soluble sodium salt in the regenerant effluent in sufficient concentration to permit recovery. The effluent is acidified to pH 5.5 to remove excess carbonate, evaporated to 15–20% malate content, and adjusted to pH 6.0. Calcium chloride is added to precipitate cal-

cium malate trihydrate of about 97% purity and with about a 90% yield. Calcium malate is then converted to the free acid by double decomposition with sulfuric acid with nearly quantitative yields.

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